



# Solvent free synthesis of organometallic catalysts for the copolymerisation of carbon dioxide and propylene oxide

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## ABSTRACT

The aim of this study was to determine the potential of using high pressure CO<sub>2</sub> as an alternative solvent for the synthesis of organometallic catalysts that can be used for the synthesis of biodegradable polymers. Zinc glutarate that is fabricated from reaction between zinc oxide and glutaric acid, is a solid heterogeneous catalyst with high efficiency for the synthesis of polymers such as aliphatic polycarbonate and polyglycidol. This catalyst is commonly prepared in a toxic organic solvent such as toluene. The yield of the reaction for the synthesis of zinc glutarate catalyst in high pressure carbon dioxide was 86%, which was comparable with the one fabricated in toluene. Processing by high pressure CO<sub>2</sub> has negligible effects on the particle size, but significant effect on zinc glutarate surface area (46% reduction) and crystallinity (12% enhancement) in crystallinity, compared with using toluene as a solvent. A catalyst with less porosity, hence lower surface area was formed in high pressure CO<sub>2</sub>. The activity of zinc glutarate catalyst produced in CO<sub>2</sub> system was increased to 74.2 g polymer/g catalyst for the synthesis of poly(propylene carbonate) compared with 67.4 g polymer/g catalyst prepared with conventional method. This effect was attributed to the substantial enhancement in the degree of crystallinity and crystal perfectness of ZnGa catalysts in CO<sub>2</sub> system. The results of FTIR and WXR analysis demonstrate the feasibility of synthesizing other organometallic catalysts such as zinc adipate in high pressure CO<sub>2</sub> with a high yield of 77.5%.

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## 1. Introduction

The use of organic solvents is extremely widespread in industry. While the degree of hazard may vary, all solvents should be considered harmful to the environment. The recent drive within society towards the use of green-technology in conjunction with the hazardous nature of organic solvents has deemed the research into finding alternative solvents for industry.

The use of organic solvents in a range of industries is associated with a generation of large amounts of liquid waste and solvent emissions, which are a cause of environmental and economic burden. It has been estimated that organic solvents in industrial processing operations release about 20 million tonnes of volatile organic solvents (VOCs) per year [1]. The amount of liquid waste created in many branches of the chemical industry is often far greater than the mass of the products, in some cases hundreds times, as in the case of the pharmaceutical industry [1].

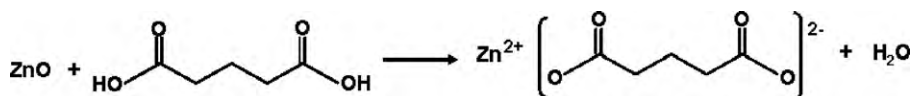
For more than 30 years, researchers seek to minimise organic solvent consumption and to replace them with benign alternatives such as supercritical carbon dioxide (SCCO<sub>2</sub>) [2], supercritical water

[2], CO<sub>2</sub> expanded liquids, ionic liquids and switchable solvents [3]. Particular attention was given to SCCO<sub>2</sub> because of the widespread view that it satisfies several green chemistry and engineering principles and has been successfully used as a media for reaction such as polymerisation [4–8], and particle micronisation [9–11]. Carbon dioxide is nontoxic, nonflammable, inexpensive and easily separated from the product by tuning process variables such as pressure and temperature.

In contrast, excessive CO<sub>2</sub> release is one of the major contributors to global warming. Carbon dioxide capture has attracted considerable attentions in recent years. One of the possible approaches is to convert CO<sub>2</sub> into polymers with tailored properties that can be widely used in industry. However, the relatively high thermal stability of CO<sub>2</sub> impedes its application as a cheap and abundant carbon source in polymerisation. A catalyst with very high activity is required for initiation and progression of the reaction for CO<sub>2</sub> polymerisation. In 1969 Inoue et al. first pioneered the copolymerisation of CO<sub>2</sub> and epoxides to produce aliphatic poly(alkylene carbonate) [12]. In the past decades, various types of catalysts have been fabricated to enhance the conversion of CO<sub>2</sub> into polymer chain [13–19]. In 1995, Darensbourg et al. successfully synthesized poly(propylene carbonate) by using SCCO<sub>2</sub> as both the reactant and reaction medium with zinc glutarate (ZnGa) as the catalyst, which is one of the most effective and cost effective

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**Scheme 1.** Production of ZnGA from zinc oxide and glutaric acid.

tive heterogeneous catalysts [20]. Zinc glutarate can be used for the reaction between  $\text{CO}_2$  and epoxide monomers [13,21,22], and the synthesis of other biodegradable polymers such as terpolymer poly(propylene carbonate-co-caprolactone) [23] and polyglycidol [24]. Zinc glutarate is not toxic and has been used as food supplement in commercial multivitamins, furthermore it is good for skin anti-aging treatment since zinc is biologically needed to catalyse the generation of collagen and elastin [25]. Therefore, the small amount of zinc glutarate residue in the biodegradable polymers was believed to have negligible effect on their further biomedical applications.

It was found that the copolymerisation of  $\text{CO}_2$  and epoxide catalysed by ZnGA involves two stages, that is, epoxide addition to a metal carboxylate with subsequent  $\text{CO}_2$  addition to a metal alkoxide alternatively [20]. For example,  $\text{CO}_2$  and PO are reversibly absorbed onto the zinc centers of ZnGA catalyst and the ring-opening of PO and double bond activation of  $\text{CO}_2$  result in the growth of polymer chain. However, PO is more easily absorbed and inserted into Zn–O bond instead of  $\text{CO}_2$ , indicating the copolymerisation is initiated by PO [21].

The activity of ZnGA catalyst was a function of zinc source and zinc oxide was demonstrated to exhibit the highest yield [21]. In order to enhance the catalyst activity, optimization of the Lewis acidity of the Zn ion centers was also attempted by introducing an electron-donating or withdrawing substituent into the glutarate ligand. However, all of the glutarate derivatives delivered lower activity than the glutarate ligand itself [22]. Therefore, ZnGA prepared from zinc oxide (ZnO) and glutaric acid (GA) has been considered as the catalyst with the highest activity for the copolymerisation of  $\text{CO}_2$  and PO.

ZnGA is commonly produced by mixing the reactants in a solvent such as toluene at a desired temperature for a certain period of time. Glutaric acid dissolves in toluene and reacts with ZnO suspended particles in slurry solution to yield the catalyst as shown in Scheme 1 [21,26,27]. The yield of 97% with a catalytic activity of 64 g polymer/g catalyst has been achieved at 60 °C within 4 h [13,22]. The purity of ZnO, stirring method and the polarities of the organic solvents were demonstrated to have significant impact on the characteristics of catalyst (e.g. crystallinity, particle shape) hence affect its activity [26,28]. Therefore, care must be taken dur-

ing the synthesis to control process parameters to influence the catalyst activity.

Our hypothesis was that high pressure  $\text{CO}_2$  could be used as a benign solvent for the synthesis of organometallic catalysts such as ZnGA, which can be used for the production of polymers. This hypothesis was corroborated by the significant solubility of solid compounds such as 2-methyl glutaric acid (2-MGA), one of the derivatives of GA, and benzoic acid (BA) in  $\text{CO}_2$  at temperatures between 35 °C and 65 °C, and pressures between 90 bar and 150 bar (Table 1) [29,30]. It can be expected that GA may possess reasonable solubility in high pressure  $\text{CO}_2$  due to its similar molecular structure and physical properties as 2-MGA.

It may, therefore feasible to conduct the suspension reaction in high pressure  $\text{CO}_2$  system. It is anticipated that the reaction can be carried out for low soluble organic groups. However, the rate of reaction may decrease due to the low concentration of reactants in the high pressure  $\text{CO}_2$ . Conducting the reaction in high pressure  $\text{CO}_2$  may also enhance the activity of catalyst, because of the effect on crystallinity or minimising the particle agglomeration and eliminating the organic solvent residue.

The effect of process variables such as temperature, pressure, reaction time, stirring method and washing procedure on the catalyst activity was determined. In this study we examined the synthesis of ZnGA and its activity in production of poly(propylene carbonate) (PPC) from  $\text{CO}_2$  and propylene oxide (PO). Some other organometallic catalysts were reported to be active for the copolymerisation of  $\text{CO}_2$  and PO, such as zinc adipate (ZnAA) [15], zinc methyl glutarate (ZnMGA) [22] prepared from the reaction between ZnO and adipic acid (AA), 2-MGA, respectively, and cobalt benzoate (CoBA) [31] produced from reaction between cobalt acetate and BA. Therefore, in our study, the synthesis of these organometallic catalysts using high pressure  $\text{CO}_2$  process was also investigated.

## 2. Experimental

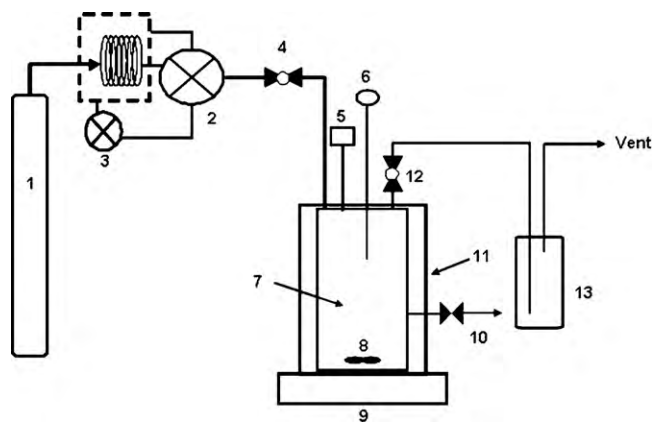
### 2.1. Materials

Zinc oxide nanopowder and glutaric acid with purity 99% were purchased from Aldrich. Before reaction, glutaric acid was ground

**Table 1**  
Solubility of 2-methyl glutaric acid and benzoic acid in high pressure  $\text{CO}_2$  at different temperatures and pressures.

Chemical	Properties	Molecular structure	Temperature (°C)	Pressure (bar)	$\text{CO}_2$ density (kg/m <sup>3</sup> ) <sup>a</sup>	Solubility (mole fraction)	Ref.
2-Methyl glutaric acid	White crystalline solid		50	97	354.6	$3.0 \times 10^{-5}$	[28]
				110	447.5	$2.0 \times 10^{-4}$	
				117	491.6	$1.4 \times 10^{-3}$	
			65	117	370.4	$1.3 \times 10^{-4}$	
Benzoic acid	Colourless crystalline solid		35	120	519.0	$1.2 \times 10^{-3}$	[29]
				100	384.4	$2.1 \times 10^{-4}$	
			50	120	510.6	$2.1 \times 10^{-4}$	
				150	699.8	$1.8 \times 10^{-3}$	

<sup>a</sup> Calculated from online software (<http://www.peacesoftware.de/einige/werte/co2.e.html>).



**Fig. 1.** Experimental setup. 1, CO<sub>2</sub> cylinder; 2, high pressure pump; 3, circulation pump; 4, inlet valve; 5, pressure indicator; 6, thermometer; 7, custom-made high pressure vessel; 8, magnetic stirrer; 9, hotplate; 10, pressure relief valve; 11, heating jacket; 12, exit valve; 13, waste trap.

up to the fine powders. Food grade CO<sub>2</sub> (>99.9% purity) was obtained from BOC Company. Solvents used in this study were all analytical grades. Toluene, methanol, dichloromethane (DCM) and tetrahydrofuran (THF) were supplied by Aldrich, acetone and absolute ethanol were purchased from Ajax Finechem and Merck chemical company, respectively. Propylene oxide with 99.5% purity was obtained from Fluka. Adipic acid (99.5%), 2-methyl glutaric acid (98%), cobalt acetate (99.995%) and benzoic acid (99.5%) were purchased from Sigma company.

## 2.2. Preparation of catalysts

Prior to conducting the high pressure experiment, ZnGA was prepared according to the conventional method as described in literature [25]. Equal molar ratios of ZnO (4.05 g, 50 mmol) and GA (6.60 g, 50 mmol) were added into toluene at 60 °C, the mixture was stirred for 4 h and the product was then collected.

The schematic diagram of the high pressure system used for the synthesis of catalyst is depicted in Fig. 1. In each experiment known amounts of ground reactants (e.g. GA and ZnO) were added into a high pressure stirred reactor with controlled temperature. The humidity may have a negative effect on particle size of the catalyst and hence its activity [32]. Prior to pressurisation, the system was purged with CO<sub>2</sub> to remove air and water residues. A high pressure pump (Thar Model 50P) was used to gradually pressurise the vessel to a desired pressure and the system was then isolated. After a set period of time, the stirring was ceased, the reactor was gradually depressurised, and the product was collected. Other catalysts prepared from the reaction between ZnO and AA, 2-MGA, cobalt acetate and benzoic acid were also obtained using the same procedure.

In both systems the residues of reactants were removed by washing the product with acetone, water and ethanol, subsequently, followed by drying under vacuum to dry the powder. The catalyst was then stored at ambient temperature in a desiccator for further characterisation.

## 2.3. Catalyst characterisation

The FTIR spectra of the catalysts were collected at a resolution of 4 cm<sup>-1</sup> and co-added 32 scans with an attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrometer (Varian 660-IR) over the range of 4000–550 cm<sup>-1</sup>. The particle size and distribution of the catalyst suspended in chloroform were determined using Malvern Mastersizer 2000. Surface area was measured by the Brunauer–Emmet–Teller (BET) technique using a

Quantachrome Autosorb-1 analyzer using nitrogen as an absorbing gas. Thermal behavior of the catalysts was examined with thermogravimetric analysis (TGA) conducted with thermogravimetric analyzer (SDT Q600) at ramping rate 20 °C/min under nitrogen from 20 °C to 600 °C. The crystallinity and crystal structure was measured by wide-angle X-ray diffraction (WXR) with step size of 0.02° over the range of 4–90° using a Siemens D5000 diffractometer with copper (Cu) k-alpha radiation with a wavelength of 1.5418 Angstroms. Field Emission Scanning Electron Microscopy (FE-SEM) was used to observe the surface morphologies of the catalysts. The samples were coated with gold and imaged with a Zeiss Ultra Plus field emission scanning electron microscope.

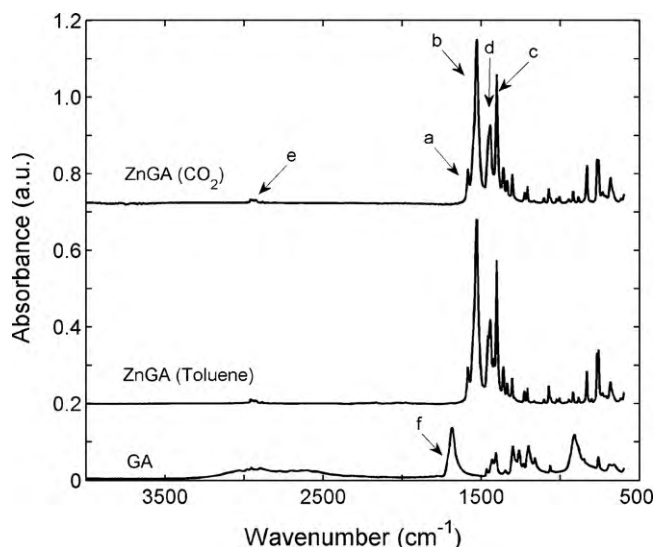
## 2.4. Synthesis and characterisation of PPC

Prior to the polymerisation reaction ZnGA (100 mg) and the high pressure reactor (25 mL) were dried at 100 °C under vacuum to remove traces of water from the catalyst and reactor. After the reactor was cooled down, 5 mL PO was then added into the vessel, followed by purging with CO<sub>2</sub> before heating and then pressurised with CO<sub>2</sub> up to the desired pressure (50 bar) at predetermined temperature (60 °C). After the certain period of time (40 h) the heater and stirrer were turned off, the system was cooled down to room temperature and the pressure was slowly released. The polymer was collected and the catalyst was then removed from the product according to the procedure described by Wang et al. [27]. The resulting polymer product was dissolved in DCM and the catalyst was extracted with dilute hydrochloric acid (5%), then the mixture was transferred to a separating funnel to remove the acid solution. The extract process was repeated triple followed by washing with distilled water. The final DCM solution was concentrated by using a rotary evaporator and the PPC product was precipitated out by pouring the copolymer solution into methanol. The precipitated product was filtered off and dried under vacuum at room temperature and the gross yield of polymer was measured by gravimetric method.

The chemical structure of polymer chain was determined with ATR-FTIR spectrometer (Varian 660-IR) over the range of 4000–550 cm<sup>-1</sup> and nuclear magnetic resonance (NMR) spectroscopic measurement by using a Bruker NMR spectrometer (DPX 400). Chloroform-*d*<sub>1</sub> (CDCl<sub>3</sub>) was used as the solvent for NMR. The molecular weight of polymers was measured by gel permeation chromatography (GPC) (Polymer Laboratories GPC-50) using THF at 1.0 mL/min as the eluent. The GPC system was calibrated with poly (methyl methacrylate) (PMMA) standards (Polymer Laboratories), with molecular weights ranging from 1020 to 1,944,000 Da.

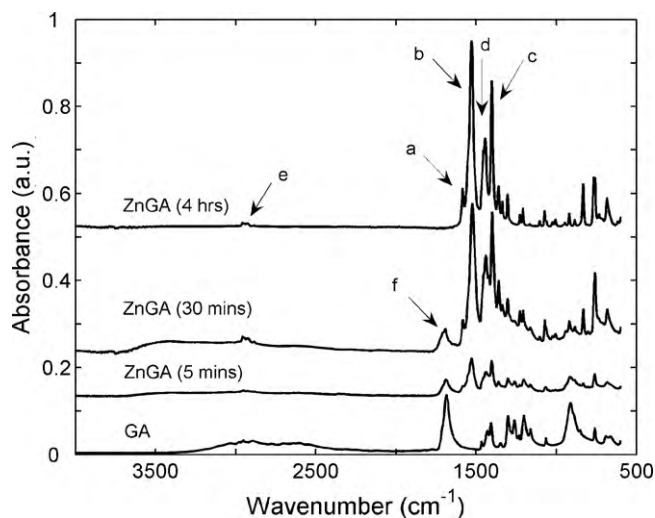
## 3. Results and discussion

The formation of zinc glutarate in high pressure CO<sub>2</sub> process was confirmed by comparing the FTIR spectra of the product with the one produced in toluene and reported in the literatures [22,26]. The FTIR spectra of ZnGA synthesized in CO<sub>2</sub> at 50 bar was consistent with the one produced in toluene and the results reported literatures as shown in Fig. 2. The absence of peak at 1697 cm<sup>-1</sup> (peak f) and presence of peaks at 1585 cm<sup>-1</sup>, 1536 cm<sup>-1</sup> and 1405 cm<sup>-1</sup> (peaks a–c) corroborates that the GA carbonyl (C=O) group converted to zinc-carboxylate bond (COO<sup>-</sup>). The absorbance of CH<sub>2</sub> scissoring (peak d) and CH stretching 2952 cm<sup>-1</sup> (peak e) was also detected. These results confirmed that the chemical structure of ZnGA produced from these two methods was identical, suggesting the feasibility of solid-based catalyst synthesis in CO<sub>2</sub>. In addition, vibrational characteristic peak of GA, which is carbonyl (C=O) stretching of 1697 cm<sup>-1</sup> was not detected in the FTIR spectrum, indicating no residual GA in the final product after purification.

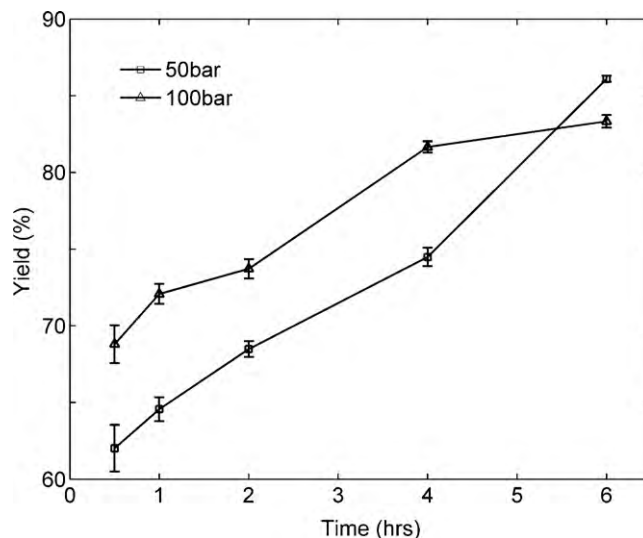


**Fig. 2.** FTIR spectra of ZnGA synthesized in toluene (60 °C, 4 h) and CO<sub>2</sub> system (60 °C, 50 bar, 4 h). Peaks a–c represents the zinc-carboxylate bond (COO<sup>−</sup>) absorbance at 1585 cm<sup>−1</sup>, 1536 cm<sup>−1</sup> and 1405 cm<sup>−1</sup>, respectively, peak d represents the carbonyl (C=O) stretching of 1697 cm<sup>−1</sup>.

The processing conditions such as reaction time, pressure, temperature, and the nature of reactants were expected to have a significant impact on the yield and characteristic of the catalyst. The time is one of the key factors on yield of reaction. The appearance of peaks at 1585 cm<sup>−1</sup>, 1536 cm<sup>−1</sup> and 1405 cm<sup>−1</sup> revealed that zinc-carboxylate bond was formed at 60 °C and 50 bar and reaction proceeded even after 5 min, however, with low yield. The peak at 1697 cm<sup>−1</sup> in Fig. 3 for the conditions that reaction carried out less than 30 min confirms the presence of un-reacted GA as an impurity in the product. This peak was not observed when the reaction time was 4 h; however this period may not be an optimum time for the reaction as other factors such as pressure and temperature may increase the solubility of GA in CO<sub>2</sub> and subsequently enhance the rate of the reaction, decreasing the processing conditions to achieve high yield.



**Fig. 3.** FTIR spectra of ZnGA synthesized in CO<sub>2</sub> system at 60 °C, 50 bar. Peaks a–c represents the zinc-carboxylate bond (COO<sup>−</sup>) absorbance at 1585 cm<sup>−1</sup>, 1536 cm<sup>−1</sup> and 1405 cm<sup>−1</sup>, respectively, peak d represents the carbonyl (C=O) stretching of 1697 cm<sup>−1</sup>.



**Fig. 4.** Effect of reaction time on the yield of ZnGA at 60 °C.

### 3.1. Effect of process variables on ZnGA synthesis

Previous studies demonstrate that stirring method slightly affects the yield of reaction for the synthesis of ZnGA in toluene. An efficient stirring device enhances the rate of reaction between the suspended solid particles and dissolved GA. Care must be taken prior to large scale design to assess the effect of stirring method on the yield of reaction. In bench scale studies, higher yield was achieved by using magnetic stirrer compared with other stirring devices such as mechanical and ultrasonic [25]. In a system using magnetic stirring, the yield of ZnGA fabrication was marginally improved from 98% to 100% when the processing time was increased from 8.5 h to 15 h [25]. In our study 95.4% ZnGA yield was achieved by using magnetic stirrer for 4 h in toluene; this catalyst was used as a reference for further characterisations.

#### 3.1.1. The effect of time

The yield is generally increased by extending the time for various types of reaction kinetics. At all conditions examined, the yield was first increased dramatically and then approached to a plateau as shown in Fig. 4. At conditions that subcritical CO<sub>2</sub> was used, 50 bar and 60 °C, the yield was enhanced from 62% to 75%, when the reaction time was increased from 30 min to 4 h. At the same period of time, when supercritical CO<sub>2</sub> was used; the yield was increased from 68% to 82%. The data in Table 1 demonstrates that the solubility of a reactant in CO<sub>2</sub> is proportional to the fluid density. Therefore, the enhancement of the reaction rate is most likely resulted from increasing the solubility of GA in CO<sub>2</sub> due to the escalated fluid density (e.g. 290 kg/m<sup>3</sup> at 60 °C, 100 bar and 98.3 kg/m<sup>3</sup> at 60 °C, 50 bar).

High solubility of a solute increases the concentration, which in turn enhances the rate of contact between a soluble reactant (GA) and dispersed solute (e.g. ZnO), therefore, promoting the rate and yield of reaction. The solubility of a chemical in a solvent is governed by their polarity, molecular weight, and the solvent density. The solvation power of a supercritical fluid can be tuned over a wide range by tailoring the pressure and/or temperature of the system. Therefore, both pressure and temperature can play a key role on the rate of reaction in CO<sub>2</sub> system.

#### 3.1.2. The effect of pressure

Pressure may have a significant impact on the yield of ZnGA. At each temperature by elevating the pressure, the density of CO<sub>2</sub>



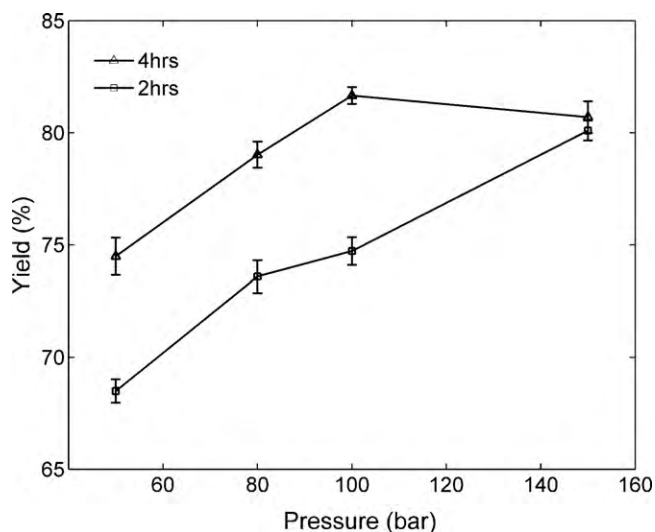


Fig. 5. Effect of pressure on the yield of ZnGA at 60 °C.

increases, hence the solubility of a solute enhances. In the synthesis of ZnGA, upon raising the solubility of GA in CO<sub>2</sub>, it is anticipated to achieve higher yield by having higher concentration of reactant. Our results are in agreement with the theory; as depicted in Fig. 5; the yield of ZnGA was promoted by increasing the operating pressure. After 2 h, the yield was only 68% at 50 bar and it was dramatically increased to 80%, when the pressure approached 150 bar. Furthermore, the yield of reaction at 150 bar for both 2 h and 4 h were the same, corroborating that at higher pressures such as 150 bar shorter period of time was adequate to achieve high yield.

At each temperature the density of CO<sub>2</sub> increases dramatically by elevating the pressure from 50 bar to 150 bar; subsequently the solubility of GA was increased. The higher solubility of GA in CO<sub>2</sub> at higher pressures described the high yield even at shorter period of time. In addition, the mass transfer properties of CO<sub>2</sub> enhances at supercritical conditions compared with subcritical [33].

### 3.1.3. The effect of temperature

Temperature has an effect on the solvation power and hence the solubility of a reactant in CO<sub>2</sub>. In addition, by increasing temperature the rate of reaction is commonly increased according to the Arrhenius equation [34]. Most of the experiments for the synthesis of GA were conducted at 60 °C to have similar reaction rate constant, to minimise the uncertainty caused by temperature variation. A set of experiments was performed to determine the effect of temperature on the yield of ZnGA in CO<sub>2</sub>. As shown in Fig. 6, at each pressure the yield was increased by raising the temperature. The effect of temperature on the yield of ZnGA was more pronounced at 100 bar than 50 bar; however, at both pressures the yield was increased monotonically by elevating the temperature. Interestingly at 40 °C, the yield of the reaction was similar at 100 bar and 50 bar regardless of the reactant concentration variation from the fluid density change (i.e. CO<sub>2</sub> density was 628.7 kg/m<sup>3</sup> and 113 kg/m<sup>3</sup>, respectively); it is suggested that kinetic of the reaction was the predominant factor at this temperature. At 50 bar, the yield was gradually increased when the temperature increased from 40 °C to 80 °C. It is, therefore, feasible to achieve higher yield at lower pressures by increasing the reaction time and also using higher operating temperature.

### 3.2. Catalyst characterisation

The yield of ZnGA at 60 °C and 4 h was 95% in toluene and 86% in CO<sub>2</sub> at 50 bar for 6 h. The 10% lower yield can be justified by using

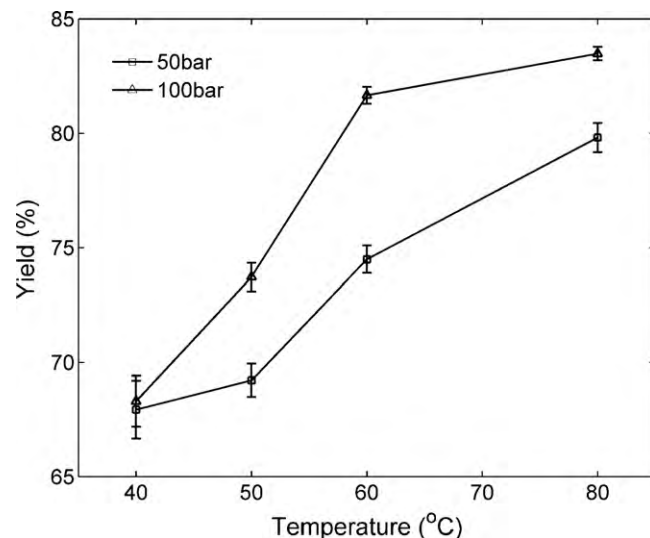


Fig. 6. Effect of temperature on the yield of ZnGA for 4 h.

a less hazardous solvent in the reaction system. The solubility of solutes in a medium is a key factor in kinetic of reaction and the final yield.

We demonstrate that the process variables have significant impact on the yield of ZnGA. The physical properties of ZnGA were measured for the samples fabricated at 60 °C. The effect of pressure and/or time on the characteristics of the catalyst was determined and several catalysts with high yield were selected for the further characterisations (Table 2).

#### 3.2.1. Crystallinity of ZnGA catalysts

The XRD analysis was used to determine the degree of crystallinity of catalyst and the presence of unreacted ZnO; the activity of a catalyst may decrease because of impurity. The glutaric acid residue can be easily washed away by acetone and water, however, due to the solubility of both ZnO and ZnGA in acidic solutions it is not practical to separate ZnO residue easily.

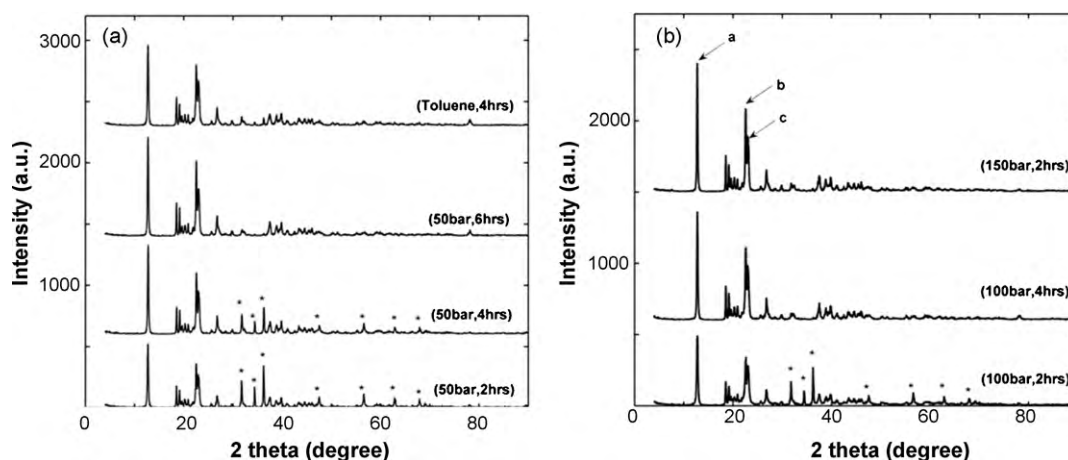
The crystal structure of ZnGA was determined by WXR and the diffraction pattern is shown in Fig. 7. At all conditions examined the WXR profiles of ZnGA were the same indicating that the crystal lattice structure was not a function of operating conditions. The WXR profile of the samples produced in toluene and CO<sub>2</sub> were comparable.

Low intensity peaks that were typical for presence of zinc oxide residues were observed in the WXR pattern of batches fabricated in CO<sub>2</sub> system at relatively short reaction time such as 2 h at 50 bar and 100 bar. The results in Fig. 7a suggest that at lower pressures, longer reaction time was necessary to achieve high yield and minimise the amount of ZnO residue; its residue was negligible when the reaction was undertaken at 50 bar for 6 h and 100 bar for 4 h. However, at high pressure such as 150 bar, the residue of un-reacted zinc oxide was low even after 2 h because of faster reaction rate (Fig. 7b).

According to the Scherrer equation (Eq. (1)), higher crystallinity and superior crystal quality including crystallite size and perfect-

Table 2  
ZnGA synthesized at different conditions.

ZnGA	Cat.T	Cat.1	Cat.2	Cat.3	Cat.4
Pressure (bar)	Toluene	50	50	100	150
Reaction time (h)	4	4	6	4	2
Yield (%)	95.4	74.5	86.1	81.7	80.1



**Fig. 7.** The effect of reaction time (a) and pressure (b) on the XRD patterns of ZnGA synthesized at 60 °C. (a–c) in (b) are the major peaks for the ZnGA and asterisks are the characteristic peaks of zinc oxide.

ness lead to sharper peaks and higher intensities. The differences of peak intensities and broadness levels observed in WXR patterns directly reflect that the catalyst crystallinity and crystal quality are function of operating conditions used for the synthesis. The peaks on WXR pattern of ZnGA fabricated at 50 bar (peaks a, b, c in Fig. 7) were sharper and stronger for 6 h reaction time than 2 h; at 2 h reaction time these peak intensities were enhanced by increasing pressure from 100 bar to 150 bar.

$$\beta = \frac{K\lambda}{L \cos \theta} \quad (1)$$

where  $\beta$  is the line broadening at half the maximum intensity (FWHM) in radians,  $K$  is a constant that varies with the method of taking the breadth ( $0.89 < K < 1$ ),  $\lambda$  is the wavelength of incident X-rays, typically 1.54 Å,  $\theta$  is the Bragg angle, and  $L$  is the mean crystallite dimension. The overall crystallinity ( $X_c$ ) was estimated with the deconvoluted crystalline and amorphous peaks of each catalyst by using curve fitting technique. The coherent length ( $L_c$ ) of crystallite was calculated from its full width at half-maximum with the Scherrer equation. Three strong peaks (peaks a–c) were selected to estimate the crystallite size and the overall crystallinity was determined from the WXR profiles.

WXR results of ZnGA catalysts synthesized by CO<sub>2</sub> process were compared with the one produced in toluene and listed in

**Table 3.** The crystallite mean dimension ( $L_c$ ), a reference that relies on crystal quality, was a function of diffraction peaks.  $L_c$  values of ZnGA synthesized in CO<sub>2</sub> (Cat.1–4) were higher than the one in toluene (Cat.T). This result underpin that replacing CO<sub>2</sub> in the reaction process remarkably promoted the crystal quality of catalyst. The overall crystallinity ( $X_c$ ) was generally higher for catalyst synthesized in high pressure CO<sub>2</sub> compared with the one produced in toluene. The lower crystallinity of ZnGA produced at 50 bar for 4 h (Cat.1) was because of unreacted ZnO that maintained as impurity in the product. In general, the degree of ZnGA crystallinity could be enhanced 10% in CO<sub>2</sub> system compared with toluene as a reaction media. As the rate of reaction was faster at higher pressures, it was possible to achieve higher degree of crystallinity at a shorter time in CO<sub>2</sub> system.

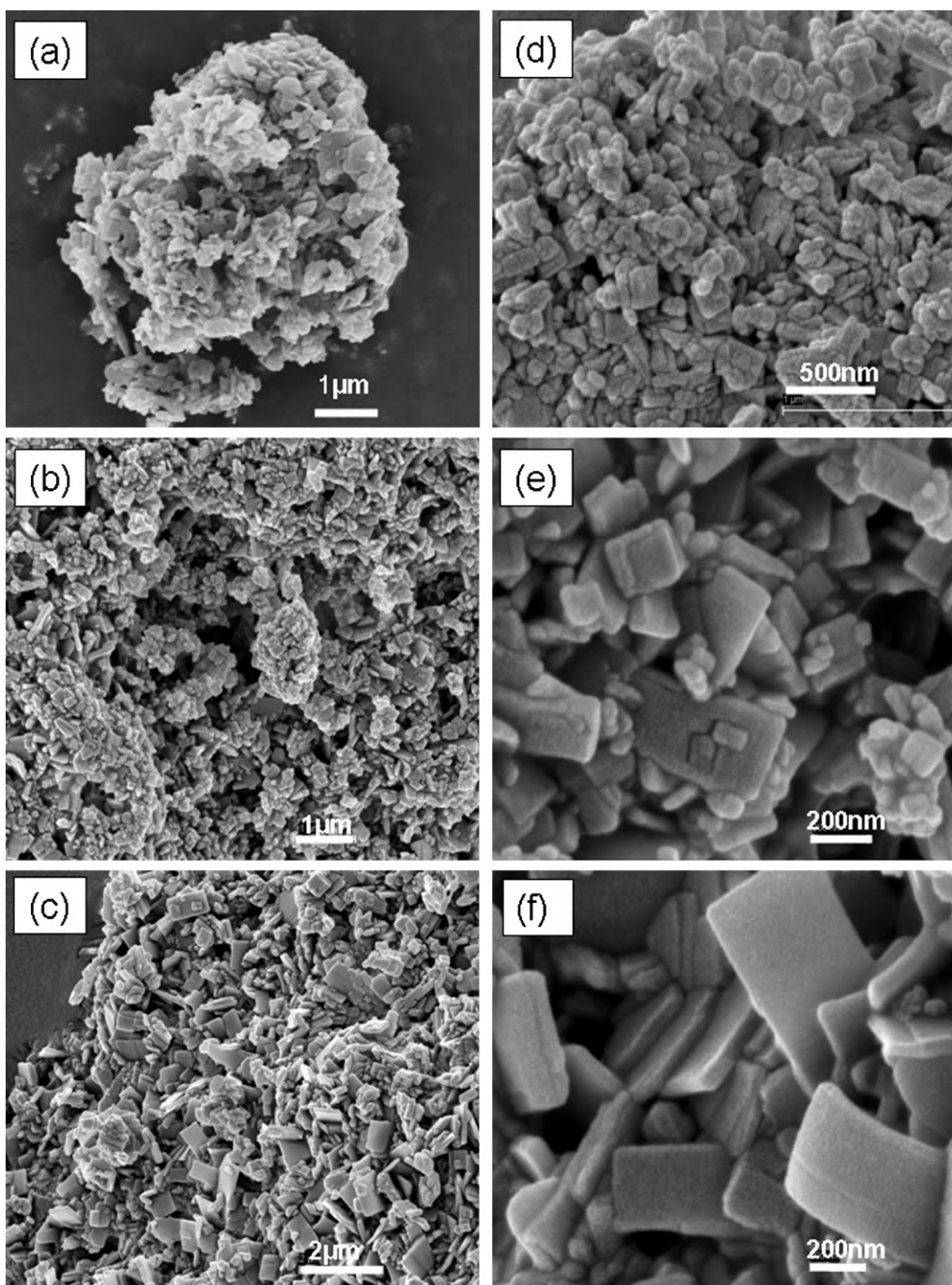
Kim et al. investigated the effect of different characteristics of a solid phase on the catalyst activity. It was suggested that the morphological structure of ZnGA including the degree of crystallinity, crystal size and shape are crucial to determine the catalytic activity [21,27,35]. Ree et al. has reported that the ZnGA catalysts prepared from various zinc and glutarate sources have the same crystal lattice structure with different crystallinities, and the ZnGA catalysts with higher crystallinity exhibited higher catalytic activity in the copolymerisation of CO<sub>2</sub> with oxirane [22]. Taking into account of these reported results and our data, it was expected that the

**Table 3**  
WXR results of ZnGA catalysts obtained at 60 °C.

WXR	ZnGA				
	Cat.T (toluene, 4 h)	Cat.1 (50 bar, 4 h)	Cat.2 (50 bar, 6 h)	Cat.3 (100 bar, 4 h)	Cat.4 (150 bar, 2 h)
Peak a					
2 $\theta$ (°)	12.70	12.74	12.72	12.74	12.72
FWHM (°)	0.26	0.24	0.23	0.23	0.22
$L_c$ (Å) <sup>a</sup>	332	363	387	385	411
Peak b					
2 $\theta$ (°)	22.52	22.56	22.52	22.54	22.54
FWHM (°)	0.34	0.32	0.31	0.35	0.30
$L_c$ (Å)	245	264	273	241	288
Peak c					
2 $\theta$ (°)	22.96	23.00	23.00	23.00	23.02
FWHM (°)	0.46	0.42	0.42	0.44	0.40
$L_c$ (Å)	180	196	199	189	206
$X_c$ (%) <sup>b</sup>	82.6	78.1	85.9	92.0	91.9

<sup>a</sup> The mean crystallite dimension ( $L_c$ ) is estimated according to the Scherrer equation.

<sup>b</sup> The overall crystallinity ( $X_c$ ) is estimated from the crystalline peaks and amorphous peaks deconvoluted for a WXR profile.



**Fig. 8.** SEM images of ZnGA synthesized at 60 °C (a) Cat.3 (100 bar, 4 h); (b) Cat.T (toluene, 4 h); (c) Cat.4 (150 bar, 2 h); (d) Cat.2 (50 bar, 4 h); (e) Cat.T (toluene, 4 h); (f) Cat.4 (150 bar, 2 h).

catalyst synthesized in the dense gas CO<sub>2</sub> system possessed superior catalytic activity or at least equivalent to the one fabricated in toluene.

### 3.2.2. Morphologies of ZnGA catalysts

The results of the field emission SEM shown in Fig. 8 demonstrate that ZnGA catalysts were generated from aggregated small-rectangular plate crystals at all conditions examined. This rectangular morphology is similar as the single-crystal ZnGA synthesized via the hydrothermal reactions of zinc perchlorate hexahydrate and glutaronitrile reported by Ree and co-workers [36]. The catalyst synthesized in toluene (Fig. 8b) presents more porous structure compared with those produced with CO<sub>2</sub> process (Fig. 8c,

d and f at higher magnifications). The crystallite size has an impact on the overall crystallinity; high crystalline catalyst (Cat.4, 91.9% crystallinity) was created from significantly larger size and more regular shape crystals compared with Cat.1 and Cat.2 with lower degree of crystallinity as shown in Fig. 8f, d, and e.

### 3.2.3. Particle size and surface area of ZnGA catalysts

The catalytic activity of a heterogeneous catalyst is mainly a function of particle size, surface area and crystallinity. Small particle size and large surface area are two critical factors that affect the catalytic activity. Our preliminary results demonstrate that the particle size of ZnGA catalyst was governed by the purification protocol and drying method. Acetone followed by water wash was



**Table 4**

Particle sizes and surface areas of the ZnGA catalysts synthesized at 60 °C.

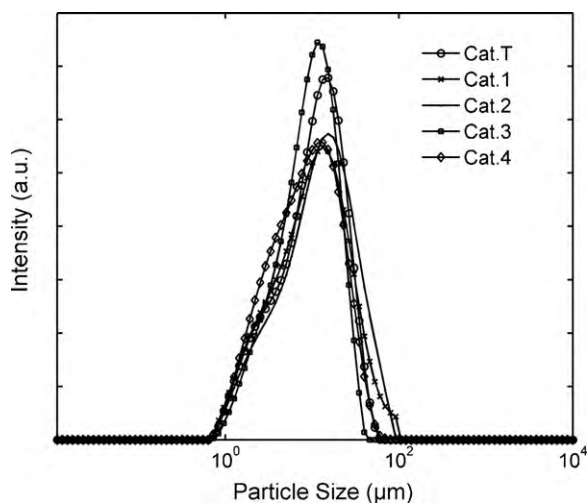
ZnGA	Particle size ( $\mu\text{m}$ )	Polydispersity ( $(D_{90} - D_{10})/D_{50}$ )	Surface area ( $\text{m}^2/\text{g}$ )
Cat.T (toluene, 4 h)	$5.61 \pm 0.12$	$2.36 \pm 0.13$	$22.05 \pm 0.18$
Cat.1 (50 bar, 4 h)	$5.98 \pm 0.02$	$2.83 \pm 0.09$	$12.05 \pm 0.11$
Cat.2 (50 bar, 6 h)	$5.38 \pm 0.07$	$3.20 \pm 0.19$	$11.92 \pm 0.10$
Cat.3 (100 bar, 4 h)	$4.90 \pm 0.16$	$2.76 \pm 0.16$	$13.63 \pm 0.12$
Cat.4 (150 bar, 2 h)	$4.76 \pm 0.04$	$2.67 \pm 0.17$	$12.01 \pm 0.11$

applied to remove the unreacted GA to improve the purity of catalyst. However, particle size larger than  $20 \mu\text{m}$  was achieved, when using distilled water wash followed by oven dry because of the heavy agglomeration caused by capillary force and hydrogen bond formation during drying protocol. It was found that washing the catalyst by ethanol followed by vacuum drying at room temperature, significantly decreased the particle size of the catalysts to  $5 \mu\text{m}$ . It is therefore critical to conduct the purification and drying protocol consistently and with a controlled manner to minimise the particle agglomeration.

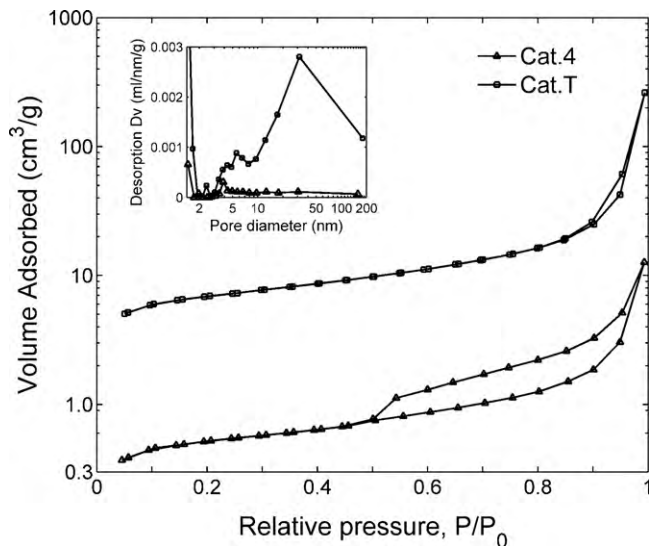
The average particle size of the catalysts fabricated in this study in both  $\text{CO}_2$  and toluene were within the range of  $4 \mu\text{m}$  to  $6 \mu\text{m}$  regardless of their synthesis conditions (Table 4). Compared with synthesis in toluene system that operates at atmospheric pressure, the particle size was slightly decreased, when high pressure  $\text{CO}_2$  was used. This result is most likely due to the lower surface tension of supercritical fluid resulting in less particle agglomeration during the reaction. The results in Table 4 and Fig. 9 demonstrate that by controlling the purification procedure, the particle size and also distribution were maintained almost constant.

The surface areas of ZnGA catalyst fabricated in toluene (ZnGA-T) was  $22.05 \text{ m}^2/\text{g}$ , however, for the one produced in  $\text{CO}_2$  system was around  $12 \text{ m}^2/\text{g}$ . It is anticipated that larger surface area is produced from smaller particles [27]. In this study the particle sizes of all catalysts were the same, however, the catalysts synthesized in  $\text{CO}_2$  exhibited significantly smaller surface areas; it might be due to the fact that at high pressure ZnGA crystals were more aggregated and highly compacted particles were formed resulting in less porosity as observed in SEM images (Fig. 8).

Total pore volume and distribution were measured to further understand the effect of synthesis conditions. Barrett–Joyner–Halenda (BJH) model was used using liquid  $\text{N}_2$  adsorption and desorption isotherm. The significantly higher



**Fig. 9.** Particle size distribution of ZnGA catalyst synthesized in toluene (Cat.T), in  $\text{CO}_2$  system with 50 bar 4 h (Cat.1), 50 bar, 6 h (Cat.2), 100 bar, 4 h (Cat.3) and 150 bar, 2 h (Cat.4). All the catalysts were produced at 60 °C.

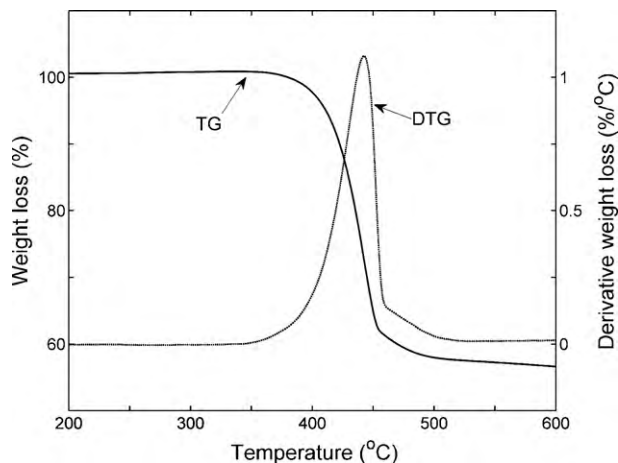


**Fig. 10.**  $\text{N}_2$  adsorption/desorption isotherms of Cat.4 and Cat.T.

$\text{N}_2$  uptake (volume adsorbed,  $\text{cm}^3/\text{g}$ ) of ZnGA synthesized in toluene (Cat.T) was observed, corroborating the larger pore volume of this catalyst (Fig. 10). Catalyst produced in toluene had more porosity with pore diameter between 5 nm and 200 nm. The catalyst synthesized in supercritical  $\text{CO}_2$  presented substantially lower  $\text{N}_2$  uptake due to the less pore volume. The major pore diameter was 2–5 nm which was the reason for the existence of the hysteresis between adsorption and desorption at high pressure according to the BJH model.

### 3.2.4. Thermal behavior

TGA analysis was carried out to assess the decomposition temperature of ZnGA produced in both  $\text{CO}_2$  and toluene. The decomposition behavior of ZnGA was commenced at 370 °C and



**Fig. 11.** Thermal gravimetric analysis of ZnGA catalyst produced in high pressure  $\text{CO}_2$ . (TG refers to the weight loss profile; DTG refers to derivative weight loss profile.)



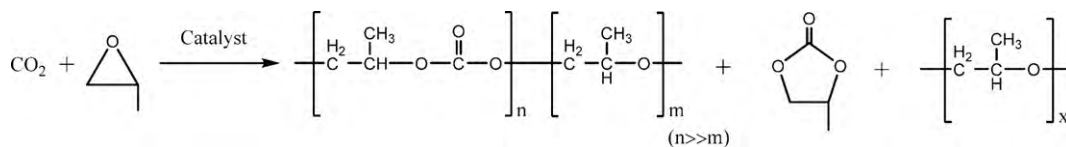
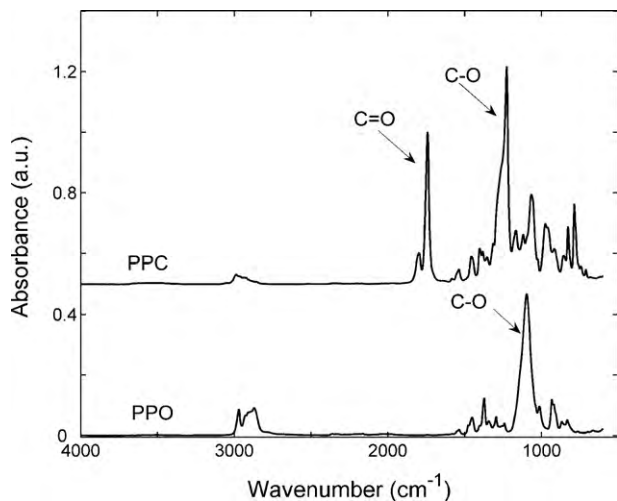
Scheme 2. Alternating copolymerisation of propylene oxide and CO<sub>2</sub>.

Fig. 12. FTIR spectra of PPC and PPO.

with 5% weight loss approached to 410 °C as shown in Fig. 11. The same TGA profile was observed for ZnGA catalyst synthesized at various conditions examined in this study. The results of thermal gravimetric analysis demonstrate that fabricated ZnGA catalyst is stable for conducting reaction at below 370 °C.

### 3.3. Catalyst activity

Higher crystallinity and larger surface area can enhance the activity of ZnGA catalysts [21,27]. The catalyst fabricated with high pressure CO<sub>2</sub> process exhibited higher crystallinity but lower surface area. In this study we examined the activity of catalyst processed at different conditions for the synthesis of poly(propylene carbonate) from copolymerisation of CO<sub>2</sub> and propylene oxide (Scheme 2) [37]. The copolymerisation was conducted at optimum condition reported in the literature using CO<sub>2</sub> at 50 bar and 60 °C for 40 h [21,38].

As shown in Scheme 2, the copolymerisation of CO<sub>2</sub> and PO with ZnGA as catalyst result in formation of PPC accompanied with cyclic propylene carbonate and polyether. Both byproducts can be easily removed due to their high solubility in methanol and low solubility of PPC in this solvent.

ZnGA synthesized in CO<sub>2</sub> was also active for homopolymerisation of propylene oxide to fabricate poly(propylene oxide) (PPO). The methanol insoluble polymer products and PPO were collected for further characterisation. The FTIR spectra of PPC (the methanol insoluble polymer) and PPO is shown in Fig. 12. The peaks at wavenumber 1742 cm<sup>-1</sup> and 1227 cm<sup>-1</sup> indicate the presence of C=O group and the C–O group vibration absorbance in the chain of PPC, respectively. The existence of peak 1096 cm<sup>-1</sup> and the absence of C=O bond absorbance suggest the formation of PPO by using ZnGA catalyst.

The polymers were further examined with NMR. Both <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for the methanol insoluble polymer products is depicted in Fig. 13: <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>), 1.31 (3H, CH<sub>3</sub>), 4.18 (2H, CH<sub>2</sub>CH), 4.98 (1H, CH<sub>2</sub>CH); <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>), 16.4 (CH<sub>3</sub>), 69.0 (CH<sub>2</sub>CH), 72.4 (CH<sub>2</sub>CH), 154.3 (OCOO). The NMR spectra demonstrate that the polymer collected was PPC. The chemical shifts of 1.16 ppm (CH<sub>3</sub>) and 3.40–3.80 ppm (1H, CH<sub>2</sub>CH) observed in <sup>1</sup>H NMR spectrum correspond to the poly(propylene oxide) (PPO) unit, for PPO, <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>), 1.14 (3H, CH<sub>3</sub>), 3.56 (2H, CH<sub>2</sub>CH), 3.40 (1H, CH<sub>2</sub>CH); <sup>13</sup>C NMR (δ, CDCl<sub>3</sub>), 17.4 (CH<sub>3</sub>), 73.3 (CH<sub>2</sub>CH), 75.5 (CH<sub>2</sub>CH) (Fig. 14).

The chemical shifts of carbons in the PPO unit were not detected in the <sup>13</sup>C NMR spectrum. Therefore, these results suggested that a very small amount of PPO unit was present in the polymer product. The carbonate content was determined via <sup>1</sup>H NMR by integrating the peaks corresponding to the protons of the PPC copolymer. The calculation was conducted using the following equation [32]:

$$fc \text{ (mol\%)} = \frac{I_{4.98} + I_{4.18}}{[2(I_{4.98} + I_{4.18}) + I_{3.40-3.56}] \times 100\%} \quad (2)$$

where *I* indicates the integration of correlated proton signals in <sup>1</sup>H NMR, which is the ratio of carbonate units to all units in the main

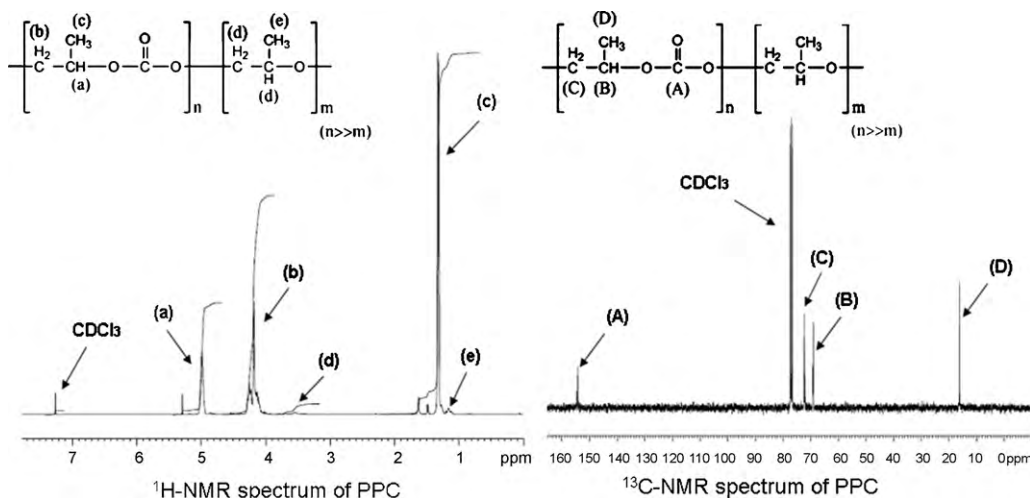


Fig. 13. NMR spectra of PPC.

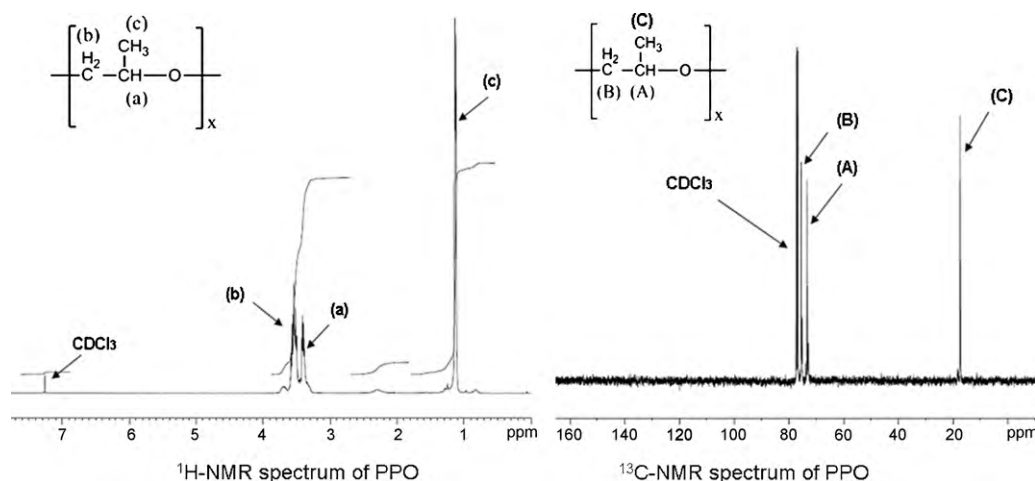


Fig. 14. NMR spectra of PPO.

**Table 5**  
Results of copolymerisation of CO<sub>2</sub> and PO.

Catalyst	Yield (g polymer/g ZnGA)	fc (mol%)	M <sub>w</sub> (kDa)
Cat.T (toluene, 4 h)	67.4	49.2	76.3
Cat.1 (50 bar, 4 h)	66.2	49.4	62.8
Cat.2 (50 bar, 6 h)	71.5	49.4	75.6
Cat.3 (100 bar, 4 h)	74.2	49.5	92.4
Cat.4 (150 bar, 2 h)	73.8	49.3	93.1

chain. Carbonate linkage (fraction of carbonate linkage, Fc) has the maximum value of 50%, for conditions that copolymerisation of CO<sub>2</sub> and PO were complete. As listed in Table 5, the concentrations of carbonate linkages in the methanol insoluble polymers were all above 49% that corroborated negligible amount of PPO present in the PPC. The weight-average molecular weights (M<sub>w</sub>) of the obtained methanol insoluble polymers (PPC) ranged from 62.8 to 93.1 kDa, furthermore, the molecular weight increased with the increase of the catalyst crystallinity rather than the surface area.

The activity of a heterogeneous catalyst is a function of its particle size, surface area and crystallinity. The yield of PPC copolymerisation was 67.4 g polymer/g catalyst when using ZnGA synthesized in toluene. It was promoted to 74 g polymer/g catalyst, when using ZnGA prepared in CO<sub>2</sub> system. The higher activity of catalyst fabricated in CO<sub>2</sub> system may be resulted from its greater degree of crystallinity. Our results demonstrated, when ZnGA surface area was increased, the crystallinity decreased and vice versa. From the results of copolymerisation (Table 5), it could be concluded that the primary factor that determine the catalytic activity of ZnGA was crystallinity. The results in the literature show when using PE6400 template solvent with proper polarity for the synthesis of ZnGA, the surface area of ZnGA was increased to 46.5 m<sup>2</sup>/g compared with the one prepared from toluene with 19.8 m<sup>2</sup>/g. However, the catalyst activity was enhanced marginally

**Table 6**  
Results of copolymerisation of CO<sub>2</sub> and PO with one-pot process.

ZnGA			Copolymerisation	Yield	
Temp. (°C)	Press. (bar)	Reaction time (h)		(g polymer/g catalyst <sup>a</sup> )	M <sub>w</sub> (kDa)
60	50	6	60 °C, 50 bar, 40 h, PO 5 mL	47.8	71.4
60	80	4		50.2	73.5
60	100	4		53.6	91.7
60	150	2		52.3	90.2

<sup>a</sup> Catalyst is a mixture of ZnGA, unreacted GA and ZnO. 0.5 mmol ZnO and 0.5 mmol GA were added in the beginning.

from 64 g polymer/g catalyst to 67 g polymer/g catalyst due to the drop of crystallinity level from 95% to 77% [28]. These results demonstrate that the degree of crystallinity and surface area play complementary roles in determining the catalyst activity.

### 3.4. One-pot synthesis of the catalyst and polymer

A one-pot process for the synthesis of the ZnGA and PPC was investigated in this study. As described in Table 6, the results show that ZnGA without further purification was active for polymerisation, however, the yield of polymerisation reaction was slightly low. This is likely due to the existence of slight impurities such as unreacted ZnO and GA. However, the one-pot process avoided using any toxic organic solvent during the synthesis and minimised the reaction steps, and therefore it is cost effective compared to current methods, and has potential for large scale polymer production.

### 3.5. Synthesis of other catalysts using high pressure CO<sub>2</sub> process

The feasibility of using high pressure CO<sub>2</sub> for the synthesis of other organometallic catalysts was assessed. Several reactants were selected, namely adipic acid (AA) and 2-methylglutaric acid (2-MGA), which were reacted with zinc oxide to produce zinc adipate (ZnAA) and zinc methyl glutarate (ZnMGA) catalysts. The other catalyst cobalt benzoate (CoBA) was also synthesized using cobalt acetate and benzoic acid (BA).

The reactions were carried out at 60 °C and 100 bar for a period of 6 h. The results of ATR-FTIR characterisation (Fig. 15) demonstrated that ZnAA, ZnMGA and CoBA were produced. The disappearance of peaks at 1684 cm<sup>-1</sup> and presence of peak 1585 cm<sup>-1</sup>, 1537 cm<sup>-1</sup> and 1412 cm<sup>-1</sup> demonstrated the consumption of acid carbonyl (C=O) group and the formation of zinc-carboxylate bond (COO<sup>-</sup>) for both ZnMGA and ZnAA. In synthesis of CoBA the absence of peak at 1679 cm<sup>-1</sup> and the presence of peak 1541 cm<sup>-1</sup> demonstrated the consumption of acid carbonyl (C=O) group and the formation of

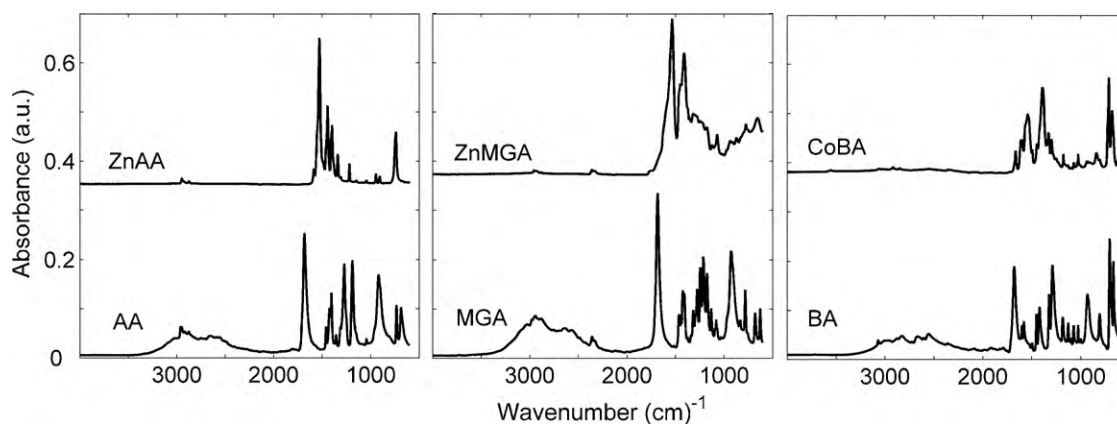


Fig. 15. FTIR spectra of ZnAA, ZnMGA and CoBA.

Table 7

Yield of synthesis of catalyst ZnAA, ZnMGA, and CoBA.

Reactants <sup>a</sup>	Yield (%)
ZnO + 2-MGA	71.2
ZnO + AA	77.5
Co(OAc) <sub>2</sub> + BA	85.1

<sup>a</sup> Equal molar ratio of the reactants (4.5 mmol:4.5 mmol) were used and reaction condition was at 100 bar, 60 °C for 6 h.

cobalt–carboxylate bond (COO<sup>−</sup>). As shown in Table 7, the yield of CoBA was higher than other catalysts, which can be attributed to the higher solubility of benzoic acid in CO<sub>2</sub> at the reaction conditions.

#### 4. Conclusions

The results of this study demonstrated that CO<sub>2</sub> can be used as an alternative solvent for the synthesis of organometallic catalysts such as ZnGA, ZnAA, ZnMGA and CoBA. The reaction was proceeding due to the solubility of one of the reactant in CO<sub>2</sub>. The yield was comparable with using toluene as a solvent. Process variables such as temperature, pressure, and type of reactants had a significant effect on the rate of reaction and yield. The reaction rate was increased by increasing the concentration of the reactant in CO<sub>2</sub>. Increasing CO<sub>2</sub> density by elevating both pressure and the reaction temperature that enhanced the kinetics of reaction, were two factors that promoted the yield of the reaction.

The particle size of catalyst was governed by the purification procedure and the operating conditions for the reaction had negligible effect on this property. However, the surface areas of the catalysts synthesized in CO<sub>2</sub> system were significantly lower than the one produced in toluene due to less porosity. All the catalysts exhibited rectangular plate morphology. Larger crystallite size with better crystal perfectness was produced in higher pressures such as 150 bar. ZnGA catalysts were thermally stable at all conditions examined and can be used for reaction at temperatures below 370 °C. The activity of the catalyst processed in CO<sub>2</sub> was 10% higher than the one produced in toluene for synthesis of PPC. The catalyst with the higher crystallinity presented superior activity compared to the one synthesized by conventional method even though it possessed larger surface area. It can be concluded that the catalytic activity primarily depends on the overall crystallinity. However, when the degree of crystallinity was the same, increasing the surface area is believed to promote the catalyst activity according to the literatures.

We established a green technology that minimised the use of toxic and carcinogenic organic solvents for the synthesis of catalyst. This process can be extended for the synthesis of other organometallic compounds with high yield and feasibility of designing one-pot synthesis of catalyst and a desired polymer in future.

one-pot synthesis of catalyst and a desired polymer in future.

#### References

- [1] EPA, Office of Air Quality Planning and Standard, E. and A.D. Monitoring, Latest Findings on National Air Quality: 2002 Status and Trends, 2003.
- [2] P.G. Jessop, B. Subramaniam, *Chem. Rev.* 107 (2007) 2666–2694.
- [3] C.-J. Li, T.H. Chan, *Organic Reactions in Aqueous Media*, Wiley, New York, 1997.
- [4] A.I. Cooper, *J. Mater. Chem.* 10 (2000) 207–234.
- [5] J.M. DeSimone, Z. Guan, C.S. Elsbernd, *Science* 257 (1992) 945–947.
- [6] J.L. Kendall, D.A. Canelas, J.L. Young, J.M. DeSimone, *Chem. Rev.* 99 (1999) 543–563.
- [7] T.J. Romack, J.R. Combes, J.M. DeSimone, *Macromolecules* 28 (1995) 1724–1726.
- [8] J.M. DeSimone, E.E. Maury, Y.Z. Menciloglu, J.B. McClain, T.J. Romack, J.R. Combes, *Science* 265 (1994) 356–359.
- [9] J. Jung, M. Perrut, *J. Supercrit. Fluids* 20 (2001) 179–219.
- [10] L.A. Stanton, F. Dehghani, N.R. Foster, *Aust. J. Chem.* 55 (2002) 443–447.
- [11] J.-H. Kim, T.E. Paxton, D.L. Tomasko, *Biotechnol. Prog.* 12 (1996) 650–661.
- [12] S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci. B: Polym. Lett.* 7 (1969) 287.
- [13] M. Ree, J.Y. Bae, J.H. Jung, T.J. Shin, *J. Polym. Sci. Polym. Chem.* 37 (1999) 1863–1876.
- [14] G.W. Coates, D.R. Moore, *Angew. Chem. Int. Ed.* 43 (2004) 6618–6639.
- [15] J.T. Wang, M.D. Shu, Y.Z.M. Xiao, *J. Appl. Polym. Sci.* 99 (2006) 200–206.
- [16] Z. Qin, C.M. Thomas, S. Lee, G.W. Coates, *Angew. Chem. Int. Ed.* 42 (2003) 5484–5487.
- [17] R. Eberhardt, M. Allmendinger, C.T. Manuela Zintl, G.A. Luinstra, B. Rieger, *Macromol. Chem. Phys.* (2004) 42–47.
- [18] R. Eberhardt, M. Allmendinger, B. Rieger, *Macromol. Rapid Commun.* 24 (2003) 194–196.
- [19] D.J. Darensbourg, J.R. Wildeson, J.C. Yarbrough, J.H. Reibenspies, *J. Am. Chem. Soc.* 122 (2000) 12487–12496.
- [20] D.J. Darensbourg, N.W. Stafford, T. Katsurao, *J. Mol. Catal. A: Chem.* 104 (1995) L1–L4.
- [21] M. Ree, Y. Hwang, J.-S. Kim, H. Kim, G. Kim, H. Kim, *Catal. Today* 115 (2006) 134–145.
- [22] M. Ree, J.Y. Bae, J.H. Jung, T.J. Shin, *Polym. Eng. Sci.* 40 (2000) 1542–1552.
- [23] S. Liu, H. Xiao, K. Huang, L. Lu, Q. Huang, *Polym. Bull.* 56 (2006) 53–62.
- [24] J.-S. Kim, H.-C. Kim, B. Lee, M. Ree, *Polymer* 46 (2005) 7394–7402.
- [25] J.R. Faryniarz, J.E. Ramirez, US Patent 20,070,184,017A1, 2007.
- [26] Y.Z. Meng, L.C. Du, S.C. Tjong, Q. Zhu, A.S. Hay, *J. Polym. Sci. Polym. Chem.* 40 (2002) 3579–3591.
- [27] S.J. Wang, L.C. Du, X.S. Zhao, Y.Z. Meng, S.C. Tjong, *J. Appl. Polym. Sci.* 85 (2002) 2327–2334.
- [28] J.-S. Kim, H. Kim, J. Yoon, K. Heo, M. Ree, *J. Polym. Sci. Polym. Chem.* 43 (2005) 4079–4088.
- [29] C.A. Eckert, F.L.L. Pouillot, B.L. Knurson, G.S. Gurdial, *J. Supercrit. Fluids* 8 (1995) 1–5.
- [30] J. Jin, C. Zhong, Z. Zhang, Y. Li, *Fluid Phase Equilib.* 226 (2004) 9–13.
- [31] M. Ree, J.Y. Bae, J.H. Jung, T.J. Shin, *Korea Polym. J.* 7 (1999) 333–349.
- [32] L.J. Gao, M. Xiao, S.J. Wang, F.G. Du, Y.Z. Meng, *J. Appl. Polym. Sci.* 104 (2007) 15–20.
- [33] L.T. Taylor, *Supercritical Fluid Extraction*, John Wiley & Sons, Inc., New York, 1996.
- [34] IUPAC, *Compendium of Chemical Terminology*, 2nd edition, International Union of Pure and Applied Chemistry, Research Triangle Park, NY, USA, 1997.
- [35] J.-S. Kim, M. Ree, T.J. Shin, *J. Catal.* 218 (2003) 209–219.
- [36] J.-S. Kim, H. Kim, M. Ree, *Chem. Mater.* 16 (2004) 2981–2983.
- [37] H. Sugimoto, S. Inoue, *J. Polym. Sci. Polym. Chem.* 42 (2004) 5561–5573.
- [38] Q. Zhu, Y. Meng, S. Tjong, X. Zhao, Y. Chen, *Polym. Int.* 51 (2002) 1079–1085.